# FATLIQUORING WITH ALKENYL SUCCINIC ACIDS*

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## ABSTRACT

A new process has been developed for lubricating chrome-tanned leathers, such as side leather, with alkenyl succinic acids (ASA). This new process permits the use of the alkenyl succinic acids in a conventional fatliquoring operation in a drum. Emulsions of ASA or ASA mixed with raw oils are produced through the use of water-soluble, high-boiling polar compounds, such as tetrahydrofurfuryl alcohol or butyl carbitol (diethylene glycol monobutyl ether), as dispersion aids. The emulsion was rapidly exhausted by drumming the stock in the oil-in-water emulsion at 50°C. (122°F.). No emulsifying agents, such as soaps or sulfated oils, were needed.

## INTRODUCTION

In recent years there has been considerable interest in developing leathers with water-repellent properties. It is generally believed that lubrication of the leather fiber is one of the important factors in producing a suitable leather substrate for this purpose (1, 2). In a recent symposium on waterproofing, sponsored by the New England Tanners' Club (1), it was pointed out that the type and amount of fatliquor can greatly influence the results of a water-repellent treatment. It was suggested that the fat content be kept to about a 5 percent level and that emulsified oils or solvent base fat liquors be used. Highly sulfated oils tend to act as wetting agents and could have a decided influence on water resistance.

Several methods are possible to introduce a limited amount of fatliquor into leather. However, when this is done, some of the desirable properties of the leather, which are dependent on the amount and type of fatliquor, may be adversely affected. Von Fuchs (3, 4, 5) described a new approach to lubrication that was attractive in this regard. He discovered that alkenyl succinic acids, referred to as ASA, were excellent leather lubricants and that only small amounts

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were needed to serve this function. This property of the alkenyl succinic acids thus appeared to offer considerable promise for lubrication of leathers to be given water-repellent treatments in general. Von Fuchs (6) had already demonstrated that this lubrication technique was desirable for a subsequent surface treatment with the same alkenyl succinic acid for producing a water-repellent leather. Other investigators subsequently reported on fundamental studies of the mechanism of the waterproofing action of the alkenyl succinic acids (7, 8).

The process recommended by Von Fuchs for lubricating with ASA comprised wringing the chrome-tanned leather to 45 to 60 percent water and then dipping the wrung leather in a mineral spirits solution of the ASA to obtain the required pick-up of lubricant (3, 4, 5). This procedure has several disadvantages from the practical standpoint as will be pointed out in the discussion. In this paper we describe a procedure for using an alkenyl succinic acid preparation (Casyl 18)‡ in a fatliquoring process, as is carried out in conventional lubrication of leather.

## EXPERIMENTAL

**Stock.**— The sides used in the fatliquoring experiments were commercially-tanned chrome grain splits, 5–6 oz. soaked back in water and drained. Sides retanned with 10 percent glutaraldehyde (25 percent solution), according to the recommended procedure in a previous publication (10), were also used. Specimens taken for preliminary studies were generally from a 6-inch strip, backbone to belly. This strip was cut into 6″ x 6″ pieces, which were prewarmed before processing with the different fatliquoring systems.

**Fatliquoring.**—The tanned stock was fatliquored with emulsions consisting of varying amounts of alkenyl succinic acid (ASA), tetrahydrofurfuryl alcohol, and sufficient water to give a 50 percent float.

**Fatliquoring with ASA Alone.**—Since the ASA (alkenyl succinic acid) is available only as a solid or viscous liquid, it is necessary to first prepare the emulsion used, as outlined below. Based on the blue weight of stock to be fatliquored, the following operation was used:

Dissolve by warming:

| | |
|---|---|
| ASA | 1% |
| THFA | 10% |

Add:

Water (at 50°C. with stirring) 40%

Add emulsion (50°C.) to prewarmed stock (50°C.)

Drum 1 hr. (emulsion is exhausted)

Horse to drain

‡Mention of brand or firm names does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

No adjustment of the system, such as the addition of acetic acid or salt to break the emulsion, was required to reach complete exhaustion of the emulsion.

**Fatliquoring with Blends of ASA and Raw Oils.**—The polar solvents mentioned above as dispersing aids for ASA are not capable of dispersing raw oils in water. However, suitable emulsions or dispersions of the raw oil did result if ASA was incorporated with the oil. A typical procedure, percentages based on blue weight, follows:

Dissolve by warming:

| | |
|---|---|
| ASA | 0.5% |
| Neatsfoot oil | 2.0% |
| THFA | 5.0% |

Add (with stirring):

Warm water (50°C.) 40%

Add warm emulsion (50°C.) to prewarmed stock (50°C.)

Drum 1 hr. (emulsion exhausts)

Horse to drain

Crust dry

The type of raw oil and the amount of ASA and raw oil in the blend can be varied over a wide range. Data for fatliquoring with blends of ASA and neatsfoot oil are given in Table I. The amount of polar solvent is not critical and may vary from five to 25 percent. However, for reasons of economy, five to ten percent is preferred.

Data obtained with the use of different types of raw oils are shown in Table II.

## DISCUSSION

Lubrication is one of the important unit operations applied to leather after tanning in order to impart certain characteristics, including strength (9, 11, 12, 13, 14). Much research has been devoted to this phase of leathermaking, and the unit process termed "fatliquoring" has become firmly established in the industry. Conventional fatliquors consist of an oil-in-water emulsion in which an oil (animal, vegetable and/or mineral or a mixture thereof) is dispersed in water by an emulsifying agent, which may be anionic, cationic, or nonionic, or blends of these. Sulfated oils, an anionic type oil, are probably the most important of the surface-active agents used in the leather industry.

In recent years, new developments in lubrication of leather have been introduced. Ushakoff (15) applied a lubricant using a non-aqueous system; i. e., an acetone solution of an oil. One of the drawbacks to this system is that special equipment is required because of the flammability of acetone and the need to

# TABLE I

## FATLIQUORING WITH COMBINATIONS OF ALKENYL SUCCINIC ACID AND NEATSFOOT OIL IN THFA — $H_2O$ SYSTEMS

| THFA* % | Fatliquor Combination* ASA % | Neatsfoot Oil % | Exhaustion | Chloroform Extractables† (Dry Basis) % |
|---|---|---|---|---|
| 5 | 0 | 1 | poor | 2.6 |
| 5 | 0 | 2 | " | 2.7 |
| 5 | 0 | 4 | " | 3.1 |
| 5 | 0.25 | 0 | good | 1.9 |
| 5 | 0.25 | 1 | " | 3.8 |
| 5 | 0.25 | 2 | " | 5.7 |
| 5 | 0.25 | 4 | " | 9.2 |
| 5 | 0.5 | 0 | good | 2.0 |
| 5 | 0.5 | 1 | " | 4.3 |
| 5 | 0.5 | 2 | " | 6.5 |
| 5 | 0.5 | 4 | " | 10.7 |
| 10 | 0 | 1 | poor | 3.8 |
| 10 | 0 | 2 | " | 2.9 |
| 10 | 0 | 4 | " | 3.5 |
| 10 | 0.25 | 0 | good | 2.7 |
| 10 | 0.25 | 1 | " | 3.6 |
| 10 | 0.25 | 2 | " | 5.8 |
| 10 | 0.25 | 4 | " | 10.4 |
| 10 | 1.0 | 0 | good | 4.7 |
| 10 | 1.0 | 0 | " | 5.3 |

*Based on drained weight of leather. Sufficient water to give a 50% float. THFA = tetrahydrofurfuryl alcohol; ASA = alkenyl succinic acid.

†Chloroform extractables of the air-dried blue stock from four locations show a range of from 1.4 to 1.9% (dry basis).

# TABLE II

## DISTRIBUTION OF LUBRICANTS IN CHROME SIDE LEATHER FATLIQUORED WITH ALKENYL SUCCINIC ACID AND RAW OILS

| Fatliquor System* | | Chloroform Extractables† | | | |
|---|---|---|---|---|---|
| Casyl 18 | Oil | Whole Leather % | Grain % | Center % | Flesh % |
| 0.5% | Castor, 1% | 4.0 | — | — | — |
| 0.5% | Safflower, 1% | 4.6 | — | — | — |
| 0.5% | Soybean, 1% | 3.6 | — | — | — |
| 0.5% | Cod, 1% | 4.8 | 7.1 | 3.1 | 5.8 |
| 0.5% | Neatsfoot, 0.5% | 4.1 | 5.6 | 2.0 | 6.8 |

*Based on the drained weight of leather; aqueous phase comprised 10% tetrahydrofurfuryl alcohol — 40% water based on blue weight.

†Reported on dry basis.

recover this solvent completely. Solvent fat liquors, which comprise conventional oils, emulsifiers, and, in addition, up to 50 percent of a high-boiling solvent (12), have been introduced recently and offer certain advantages since they may be applied in conventional equipment. As mentioned earlier, Von Fuchs developed a novel lubrication for leather involving dipping wrung blue stock in a solution of an alkenyl succinic acid in mineral spirits, which is not fatliquoring in the usual sense of this unit process. While the Von Fuchs process offers certain advantages in lubrication, it is characterized by several inherent disadvantages when considered from the practical standpoint of commercial practice. The water content of the stock is a critical and important factor and must be carefully controlled. Secondly, each side must be handled individually; i. e., the process is not operable in a drum. Attempts in our laboratory to apply Von Fuchs' lubrication principle by drumming chrome-tanned stock with a mineral spirits solution of ASA have been entirely unsuccessful. A thick cream or gelatinous mass was formed that remained on the surface of the leather and clung to the sides of the drum. Little penetration of the ASA into the fiber resulted, and uniform lubrication was not effected. This behavior is not surprising in view of Neher's observation that the alkenyl succinic acids of long-chain length are effective water-in-oil emulsifiers (8). In this system it was evident that water in the stock, especially in a conventional drumming process, would cause the emulsion to break on the surface of the leather and give little penetration and lubrication.

We have discovered how suitable oil-in-water emulsions or dispersions of the alkenyl succinic acids can be prepared and used in a conventional fatliquoring process. Emulsification was achieved by including in the mixture certain water-soluble, high-boiling polar organic substances. Only a minor amount of this polar substance is needed, less than 25 percent (generally about 10 percent) of the amount of water taken as the dispersing medium. Thus, these may be looked upon as dispersing aids, and fluid oil-in-water emulsions can be made of either liquid or solid types of ASA. However, a long-chain alkenyl substituent is required in the structure of the alkenyl succinic acid (ASA). Most of our work was with Casyl 18, an alkenyl succinic acid in which the alkenyl group (R) contains an average of 18 carbon atoms in the general structure below:

$$\begin{array}{l} R\text{—}CHCO_2H \\ \quad\;\; | \\ \quad\;\; CH_2CO_2H \end{array} \qquad \text{where } R = \text{octadecenyl}$$

Various water-soluble, polar, organic compounds can be used as dispersing aids in producing the oil-in-water type emulsions of the ASA. We have preferred to use tetrahydrofurfuryl alcohol or diethylene glycol monobutyl ether. Other water-soluble organic substances that may be used in place of the two specific compounds mentioned above are various monoalkyl ethers of diethylene glycol or dipropylene glycol, certain polyethylene glycols, and diacetone alcohol. These substances are all water-soluble and perhaps serve as effective dispersing agents by altering the solubility characteristics of the ASA in the aqueous phase.

The emulsions of ASA or of blends of ASA with raw oils are very easily prepared using the polar dispersing agents mentioned above. Stable emulsions resulted from ASA alone, or mixed with raw vegetable or animal oils. These emulsions were readily and completely exhausted under ordinary fatliquoring procedures; i. e., drumming the stock for a short time (one-half to one hour) at a temperature of about 120°F. in a short float (40 percent). Analysis of the lubricated leather (chloroform extractable, Tables I and II) showed that extracted fat was about equivalent to total fat used in fatliquoring the stock (assuming 60 percent moisture in the wrung stock). Distribution of oil (Table II) also seemed to follow normal patterns.

Lubrication of leather with ASA by this new technique offers several important advantages. In the first place, the conventional drum fatliquoring process can be used, with its advantages from equipment and materials handling standpoint. Conventional equipment is perfectly suitable for use. A second advantage lies in the fact that the moisture content of the stock is not critical. Wrung or drained stock was fatliquored very easily, and distribution of the oil was good as judged by a stain on a cut edge. A further advantage is inherent in the process because of control of the uptake of oil by the stock. Since the emulsion is exhausted, the oil uptake is regulated merely by the amount introduced into the drum. This is not the case in the lubrication process involving dipping of the wrung stock in a mineral spirits solution of ASA, where water content of the stock is a critical factor. One of the important features of this new fatliquoring process is that a free fatty acid, rather than a soluble soap, serves as the surface-active or emulsifying agent. Thus, fatty material or oils are introduced into the leather fiber without simultaneously depositing hydrophilic or water-soluble components as well. This condition therefore makes such a lubrication procedure attractive from the standpoint of water-repellent treatments since Von Fuchs has already demonstrated that leather lubricated with ASA by his procedure (3, 4, 5) can be made water repellent by subsequent surface treatment with ASA (6). This new procedure was a decidedly improved technique for lubrication with ASA, either alone or mixed with raw oils, and has been successfully applied for fatliquoring chrome-tanned side and chrome sides retanned with glutaraldehyde.

## SUMMARY

A new process for lubricating leather with alkenyl succinic acids (ASA) by a conventional drum fatliquoring process was developed. In this process, oil-in-water emulsions of ASA are produced through the use of water-soluble, high-boiling, polar compounds as dispersion aids. Based on blue weight, about one quarter to 2 percent ASA is dispersed in ten percent tetrahydrofurfuryl alcohol

(or diethylene glycol monobutyl ether) and 40 percent water. This emulsion was rapidly exhausted by drumming the stock (one half to one hour) in the emulsion at 120°F. (50°C.). The emulsion systems investigated consisted of ASA alone or ASA mixed with raw oils and contained no emulsifying agents, such as soaps or sulfated oils.

The process has been applied to chrome-tanned, as well as chrome-tanned, glutaraldehyde-retanned side leather.

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## DISCUSSION

PRESIDENT MEO: Thank you, Mr. Hopkins. Not only have you done a fine piece of work, but you have made one of our more irrepressible members, George von Fuchs, very, very happy — and that's something. Now we are open for discussion.

MR. H. R. MILLER (Pfister & Vogel Tanning Co.): I think we all agree that the health of our industry is becoming more and more dependent upon continuous improvement of our product and its properties, especially in light of the fact that the consuming public is becoming more and more critical, whereas they used to be complacent about it and say, well, this is the way leather is supposed to act. I think this paper is another tool to help us continue to improve our product.

I have just a couple of questions to throw at Mr. Hopkins before we turn the discussion over to the floor:

What is the mechanism of the improvement in ability to render a leather water repellent that glutaraldehyde gives? Also, is five percent necessary? Would two percent do it, or would ten percent do it better?

Mr. Hopkins: We think that glutaraldehyde may be important from several standpoints. Some of these may be speculative.

One is, it makes the leather fiber softer. If you make leather softer, it reduces the pumping force that you have in a flexing action. I feel this is an important factor. It also allows us to make a softer leather with less fatliquor, which is also what we are trying to do.

Also, the glutaraldehyde tannage may increase the receptivity of the fiber to subsequent treatments. For example, if your fiber isn't amenable to the treatment, penetration may be a problem. The retannage may help fibers to be wet by subsequent treatments and may improve adhesion of the water-repellent agent.

As far as the amount of glutaraldehyde is concerned, we have thought about using less, but we just arbitrarily used five and ten percent of the commercial solution, which is an aqueous 25 percent solution. There appeared to be little difference in the results between these amounts of glutaraldehyde. We ran no tests using two percent glutaraldehyde.

Mr. H. R. Miller: Thank you.

The only mention of the lubricating material was ASA. Which one was used? There have been several on the market that I know. There is Bavon, there is Casyl, there is Shellcor; there may be others. Which one was used, is it available, or, would one of the others be suitable?

Mr. Hopkins: In our work we used Casyl-18, which is available from Humphrey Wilkinson Company. This material is an alkenyl succinic acid with an average of 18 carbon atoms in the alkenyl group. Presumably other products of this structure would be equally suitable.

Dr. George von Fuchs: My comments may take the length of another paper paralleling this, but I shall not be tempted to do that.

I should like to point out the reason why alkenyl succinic acids work and fat liquors don't. Ten years ago Dr. Herfeld, in his paper entitled, "Uber den Einfluss von Netz-Emulgier und Fettlickerprodukten auf die Wasserzugigkeit des Leders," introduced the concept that certain lubricants for leather, also certain wetting agents used in wetting the leather, remain attached to the fibers and impair any attempt at waterproofing.

As a result of his work, which I referred to in my paper delivered in Vienna some eight years ago, the people who made leather waterproof by silicones or by Scotchgard religiously kept away from excess oil, because we know not only that fatliquor is a wetting agent itself, but the oil tolerance of these compounds is low. So, all the leathers you are buying today, treated with silicones, are essentially underlubricated. This paper is the first instance where it could be shown that a lubricant is available that is not adverse to the effect of waterproofing agents.

So, if I may say, in a few words, the reason why ASA works and fat liquors don't is that it is compatible with any waterproofing agent, including ASA itself. I have gotten as many as a half-million flexes on leather received from the Eastern Regional Laboratory in Philadelphia — one sample, 200,000 flexes with very low water pickup. This leather, I feel, has a great future.

We're talking about the comfort factor. What we should have in a leather is water vapor absorbability on the flesh side and liquid water barrier on the grain side. This we have in the above combination.

So, to repeat, the problem with waterproofing is to choose the proper lubricant which does not interfere with the Quilon or Scotchgard or Silicone or ASA. ASA is less susceptible to oils than the others. But in any case, in order to make a good waterproof leather, a leather which is kind to the foot, which absorbs the water vapor in a vapor form without first letting it condense to the liquid state, is the leather we want. It fulfills the requirements of a comfortable shoe which absorbs water vapor without first liquefying it.

I'm grateful to have been given the chance to check some of these results, and I have some samples of both straight chrome and glutaraldehyde retanned leathers, which are exceptionally soft and exceedingly responsive to waterproofing, and also have a good break. For understandable reasons, I am definitely in favor of a wring and dip process, or something similar to it, over a drum process. I want to be frank about this, because I had very little luck with drum applications. There has been a process developed in England which permits the application of ASA in a drum, in a fatliquor process. It involves a temporary increase in the pH of the surface of the leather, so it will not cause the compound to precipitate on the surface but permits it to penetrate. Then after lubrication is accomplished, the pH is again returned to 3.5. In other words, it can be done.

It doesn't overcome one great drawback of the fatliquor drum process. The drum process has the habit of concentrating the oil in the looser parts of the hide. Consequently, it's very much more difficult to waterproof leather which has been fatliquored by any process, even ASA. Since we have the reactivity of the collagen to contend with, we found, if you apply excessive lubricant, the tendency to looseness will be emphasized. This fact also explains the wide variety in test results reported in the paper.

My dipping process overcomes the break problem, which is very important in making a tight leather. Glutaraldehyde retannage is one way of getting a tight leather, if you don't drum the lubricant into it. Another one is melamine resin or a combination of it with magnesium aluminum lignosulfonate. All these retanning processes are conducive to making a tight leather.

I want to thank the author and his co-workers for writing this paper and for the cooperation they showed in giving me a chance to look at it before the presentation. I am all in favor of the process. Glutaraldehyde is one of the coming things.

QUESTION FROM FLOOR: Mr. Hopkins, you stated before, one of the possible reasons for the good water repellency of glutaraldehyde retanned leather is the wetting-out effect glutaraldehyde might have. It makes the fiber more responsive to wetting out. How about the replacements in that respect? Would you expect the same results?

MR. HOPKINS: Other retannages may be effective, but we didn't have time for such a comprehensive study.

MR. H. R. MILLER: We are starting to encroach upon the next speaker. If any of the other members of the audience have more questions for Mr. Hopkins, I'm sure he would be happy to have a discussion with you privately.